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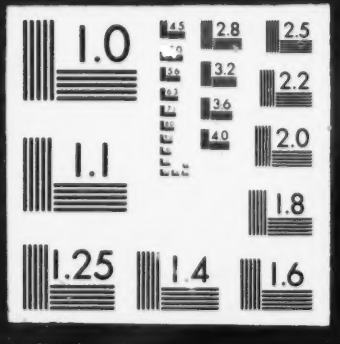

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R. B. Dean, et al

Federal Water Pollution Control Administration
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HYDROLYSIS OF ACTIVATED SLUDGE

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Many pollution experts agree that the limiting operation in a modern sewage disposal plant is the disposal of the solids which accumulate as a result of various separation procedures. Of particular concern is the disposition of activated sludge which is the solids residue resulting from aerobic digestion of soluble or non-settleable solids in sewage. It is composed of very hygroscopic microbial cells and cellular material which exists as a gel-like mass having a very low solids content, and it is most difficult to filter or settle.

Various processes have been suggested to aid in the thickening and clarification of these aerobic residues. These include addition of chemical coagulants and precipitants such as ferric chloride, polyelectrolytes, lime, alum and others. Other treatments have evolved which involve "conditioning" the settled sludge before filtration. The purpose of these treatments is to reduce the water content of the "filter cake".

An improved process for the treatment of activated sewage sludge has been developed by the Federal Water Pollution Control Administration with the contract work being conducted in the laboratories of Foster D. Snell, Inc. The process consists of heating activated organic sludge in the presence of water and small amounts of sulfur dioxide. This treatment increases soluble solids, improves filtration efficiencies by a factor of 100 and reduces the moisture content of the resultant filter cake. Concentration of the filtrate produced a molasses-type syrup which, from amino acid analysis and rat feeding studies, could be of value as an animal feed.

The general concept of wastewater disposal can best be pictured as a repeating process of solid-liquid separations and oxidations, with an aim toward producing pure water, inorganic salts and gases as the ultimate end products. This is graphically illustrated in Figure 1, which represents the cycles and oscillating systems of unit operations involved in the basic concept of disposal. Most currently-used disposal processes involve unit applications selected from the various types used elsewhere in the chemical process industry.

Over the years, waste disposal experts found that many of the improvements and sophistications of their processes increased costs, particularly in regard to the disposal of the solid residues. The rising costs of land, in and around urban centers, has made land disposal costs prohibitive. At the same time, public clamor for increasingly purer effluent water has spurred the development of improved treatments which produce even greater quantities of solid waste.

Current disposal of sewage plant solids has now become part of an operation called "ultimate disposal". Ultimate disposal deals with the problem (along with others) of disposal of refractory (resistant to oxidation) organic residues of typical biological oxidations. Sludge may be disposed of in any one of the states in which it is produced, i.e., as wet sludge (both raw and digested), filter cake, sludge cake from air-drying beds, and heat dried sludge. Methods of disposal include discharge into sewers, lagooning, dumping at sea, land fill, etc. However, engineers try to recover some of the disposal costs by selling their end product. Historic attempts have resulted in products such as

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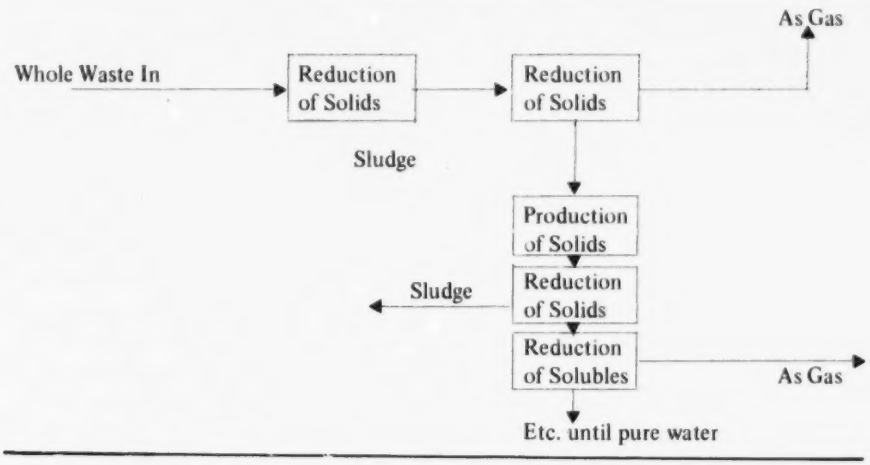
FIGURE 1
Concepts of Advanced Waste Treatment



Milorganite[R], a fertilizer composed of dried activated sludge. But the use of sludge as fertilizer has decreased because this fertilizer, which is a result of biological oxidations, is non-competitive with ammonia as a nitrogen source. Some disposal plants find it impossible to recover freight costs, let alone process costs, when they attempt to sell sludge as fertilizer. Their high costs are usually attributed to the expense of dehydrating the low solids sludge.

To overcome this cost of dewatering and dehydration, various conditioning processes have been proposed to increase the rate of filtration and to decrease the moisture content of the cake after it is formed. One such conditioning process is known as the Porteus Process (1).

In this process direct injection of steam into a thickened suspension of activated sludge supposedly alters the colloidal nature of the sludge and allows easier filtration and increased efficiency of water removal.

Another procedure suggested for processing sludge is the Zimpro Process (2), involving high pressure, wet air oxidation which converts the organics to carbon dioxide, and recovery of the energy evolved during processing. This process is efficient, but requires expensive equipment to maintain the necessary high pressures. Teletzke et al. (3) describe a modified wet air oxidation process utilizing lower pressures.

These digestions, as described, are essentially *hydrolytic* reactions involving a minimal of oxidation, and the resultant solutions are recycled to the biological system

Sulfurous Acid–a Unique Hydrolytic Agent

The use of dilute sulfurous acid as a hydrolytic and extraction agent is well known. Sulfurous acid functions especially well for solubilizing naturally-occurring substances because it provides both the acidity required and inhibits the formation of brown addition products usually referred to as humins. A whole technology has been built on the use of sulfite for delignification of pulp for the paper industry (4). Mackinny (5) reported on the efficacy of sulfurous acid for the preparation of white soya protein extracts in 1949.

Baker et al. (6) undertook a careful study of the sulfurous acid hydrolysis of casein making special note of its effect on the tryptophan content of the humin-free extract. Results showed that SO_2 hydrolysis protects the tryptophan present in hydrolysates.

In the packing house industry, a process often used to digest inedible animal residues, is a wet-rendering process, whereby hair, feathers, meat scraps, bone, etc. are cooked at relatively low pressures (60 lbs steam) for digestion and fat recovery and the preparation of specialty protein foods (7). In many cases sulfite is added to the digestion tank in the form of SO_2.

The meat-packing industry does not use SO_2-rendering as a means of disposal but as a highly efficient procedure for recovery of industrial fat and protein and for protein hydrolysis as exemplified in the manufacture of culture media universally used in commercial fermentations, such as Wilson's B-407 Peptone.

In general, the advantage of sulfurous acid as a hydrolytic agent can only be fully realized in treatments of heterogeneous natural substances containing both polysaccharides and proteins.

This paper describes the results of a research program in which we have applied techniques of hydrolysis and solubilization of meat scrap to the solubilization of activated sludge.

THE HYDROLYTIC PROCESS STUDY

Establishing Basic Parameters of Hydrolysis

A preliminary experiment was performed to establish hydrolytic parameters. For this purpose, dried activated sludge from the Chicago Sanitary District was weighted into glass jars. The samples of sludge were introduced into pint-size, Ball-brand Mason jars sealed with rubber gaskets and wire-clamped glass lids and autoclaved in a horizontal pressure device capable of maintaining up to 200 psi (Figure 2). The contents of the sample jars were adjusted to contain 200 ml of a mixture of sludge, water and sulfur dioxide (added as a solution of 3.9% SO_2). Each jar contained 6% dried sludge. This latter concentration was chosen because previous multiple tests indicated that the activated sludge from the Bergen County Sewerage Authority Plant at Little Ferry, New Jersey (the model plant for this study) averaged 4 to 5% solids over a period of several months.

The extent of solubilization (or hydrolysis) was measured by filtering the reacted slurry and evaporating 50 ml of the clear filtrate to dryness and weighing the residue. The results of this experiment are shown in Figure 3.

Operating Conditions

All sludge samples (unless otherwise noted) were treated for one hour under 30 lbs. steam pressure (140°C). Where sulfur dioxide was used, final concentration of SO_2 was 0.5% based on total mixture.

Tests were conducted on fresh activated sludge obtained from the aforementioned Bergen County Plant. It is a thickened suspension of sludge of the type normally shipped from this plant in barges for disposal. Bergen County thickens its sludge by natural settling; no chemicals are used.

The average solids content of the thickened sludge was determined by evaporation to dryness. At the same time, the soluble and insoluble solids were determined by filtration. The liquid portion was colloidal in nature and resembled blood serum.

Analysis of the sludge in repeated samples resulted in the following average

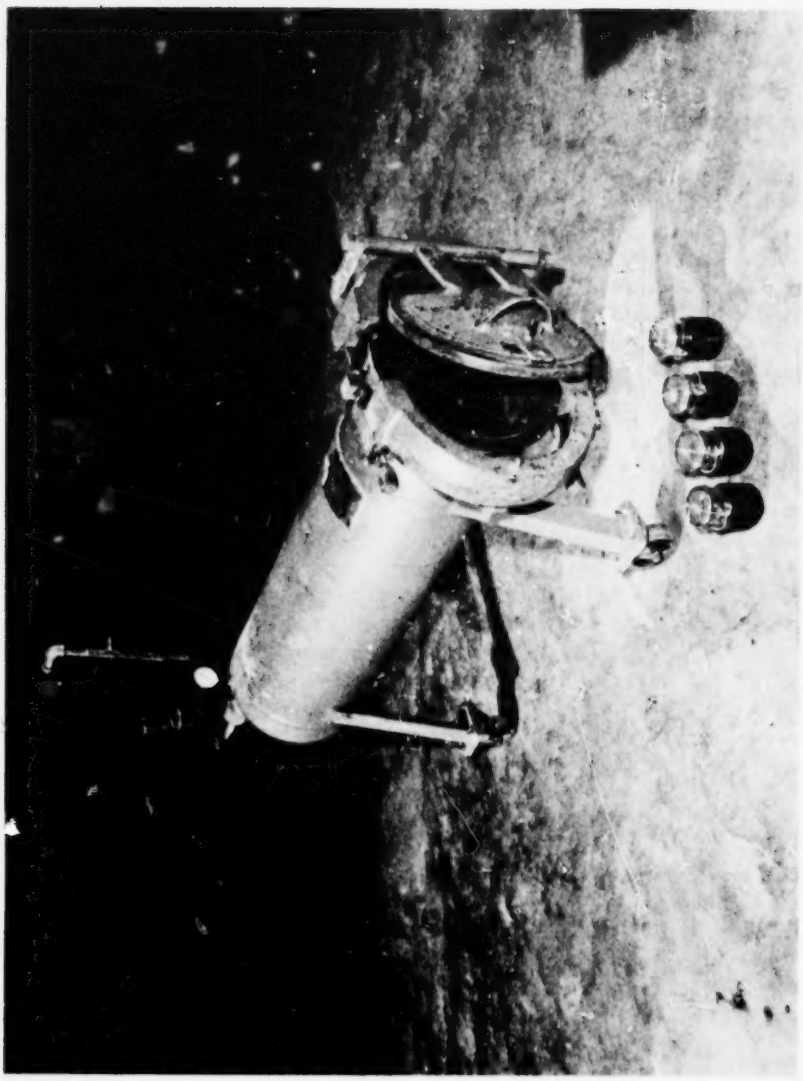


Fig.2 . Autoclave and Jars Used in the Hydrolytic Process Study

FIGURE 3
Grams of Solids in 50 ml of Hydrolysis Liquor
Prepared under Various Conditions

SO_2 Concentration	Solids in 50 ml		
	1 hour @ 100 psi	6 hours @ 15 psi	1 hour @ 15 psi
No SO_2 Added	--	0.51	0.21
.33% SO_2 Added	1.18	0.64	0.44
.63% SO_2 Added	1.21	0.68	0.48
1.2% SO_2 Added	1.38	0.96	0.48
2.5% SO_2 Added	1.47	1.41	0.71

Note: Total available solids in 50 ml would be three grams

Results: Almost 50% of the solids from dried activated sludge can be solubilized while simple cooking solubilizes only a small percentage

specification:

FIGURE 4
Analysis of Fresh Activated Sludge
Bergen County Plant

pH	6.8
moisture	91%
insoluble solids	4.18%
Soluble solids	4.82%

Filtration Studies

Separating the solids from the untreated thickened sludge was both time-consuming and tedious requiring as long as 24 hours filtration to obtain a dry cake. Hence, it was decided to treat the thickened sludge directly and measure the effect of hydrolysis by comparing the soluble solids content of the filtrate before and after treatment. The values so obtained, and compared with the total solids content of the original sludge, will be a true measure of the extent of solubilization of the colloids.

Test samples consisting of 500 gm of thickened sludge, having an average insoluble solids content of 4.18% by weight, were sealed in pint-sized Mason jars and placed in the autoclave described earlier. The samples were divided into three groups of 25 samples each and subjected to treatments A, B and C below.

FIGURE 5
Sludge Treatments

Treatment Designation	
A.	Untreated raw activated sludge
B.	Raw activated sludge autoclaved for one hour under 30 lb. steam pressure, in accordance with arbitrary parameters, and
C.	Raw activated sludge containing 0.5% by weight of sulfur dioxide added as 4.6% sulfurous acid subjected to the same heat treatment as B.

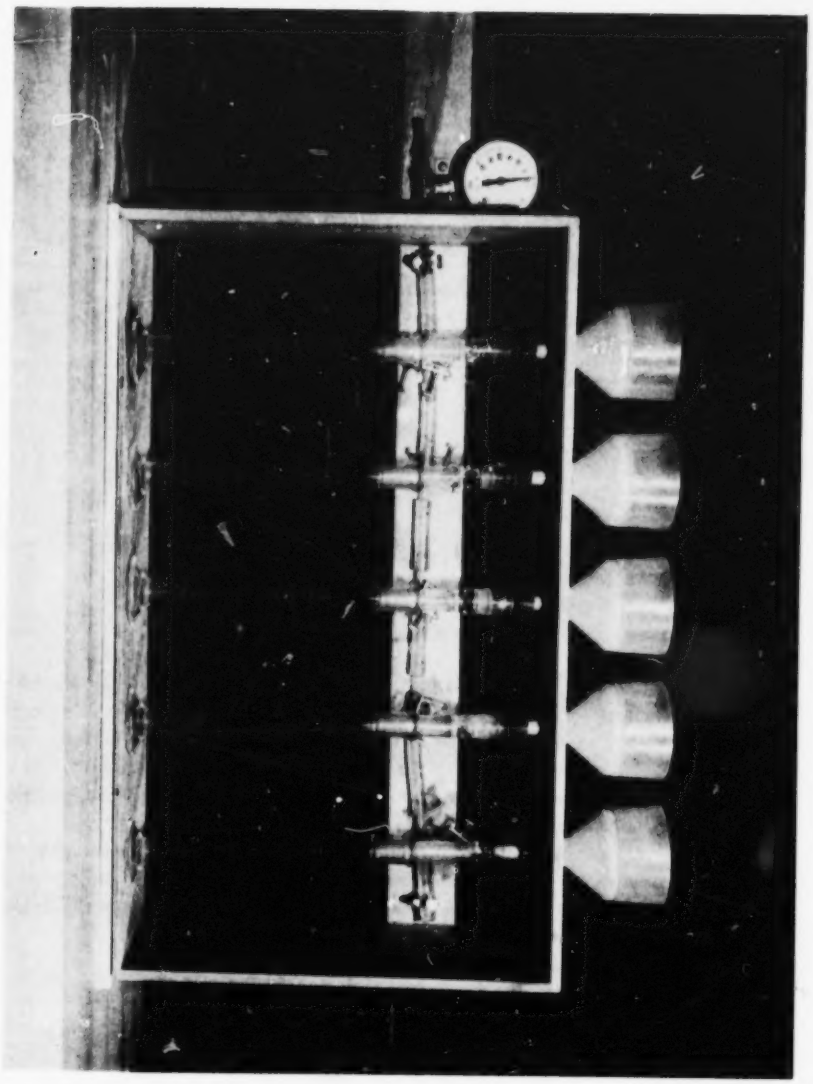


Fig. 6. Filtration Equipment used in Sludge Treatment

After cooling to room temperature, 100 ml of each sample was filtered through Whatman No.1 analytical filter paper using a battery of six Buchner funnels with a common vacuum manifold (Figure 6). The average filtration rate was determined by measuring the volume of liquid collected in 40 seconds and is summarized in Figure 7.

FIGURE 7
Filtration Rate of Treated and Untreated Sludge

Treatment	Volume of Filtrate Collected
	(ml)
A.	15
B.	40
C.	90

The filtration rate of activated sludge is increased almost three-fold by heat treatment alone, but six-fold when sulfur dioxide is added to the activated sludge before heat treatment.

A second series of tests was performed to measure the effects of heat and SO_2 treatment on the absolute rate of dewatering. The same procedure was used as in the previous experiment except that the rate of filtration was determined by noting the length of time required to reach a dry cake (by dry cake we mean the point at which no additional filtrate was obtained). In this series of experiments, 200 ml samples of sludge, treated and untreated, were filtered and both the volume of the filtrate collected and the time required to achieve a dry cake were measured. Results are summarized in Figure 8.

FIGURE 8
Absolute Rate of Dewatering

Treatment	(200 ml sample) Filtrate Collected	Time to Achieve a Dry Cake
	(ml)	(min)
A.	147	420
B.	150	4
C.	175	2

The foregoing illustrates that filtration time is reduced drastically by both heat treatment alone or heat plus sulfur dioxide. But, the amount of moisture retained in the filter cake from the sludge treated with SO_2 is reduced drastically.

The Hydrolytic Effect

It is difficult to measure accurately the real solubilizing effect of treatment with SO_2 and heat because of the difficulty in adequately dewatering the untreated sludge. This difficulty was overcome by carrying the filtration to completion and measuring the solids content of the filtrate.

FIGURE 9
Effects of Treatment on Soluble Solids Content of Filtrate

Sample	Treatment	Soluble Solids Content
		%
A.	No Treatment	4.82
B.	Heat Alone	7.34
C.	Heat + .5% SO_2	8.84

Results in this case indicate that heat treatment alone increases the soluble solids content by nearly 90% and an additional increase is obtained by addition of SO_2.

Analysis and Procedures for Prepatation of Organic Molasses

Hydrolysis of organic materials has historically been used as a process to make available otherwise undigestible food ingredients. After hydrolysis, the solubilized material is often concentrated to a thick syrup resembling the concentrated residues from cane sugar manufacture, called molasses. In the case of wood, citrus, pineapple, sorghum and many other syrups, the term "molasses" is used because it best describes the heterogeneous nature of the syrup, regardless of its original source. Thus, terms are used such as wood molasses or soy hydrolysate molasses, etc.

Currently molasses types sell for from two to five cents per pound. Manufacture of organic molasses, as a means of ultimate disposal and selling within the range of $40 to $100 per ton leaves a profit opportunity not previously exploited.

A 10-gallon sample of thickened activated sludge was collected from the outfall of Bergen County, New Jersey disposal plant. The sludge had approximately 9% solids, half of which was insoluble.

This creamy slurry was charged into a closed jacketed, 20-gallon stainless steel vessel equipped with a mechanical agitator. The equipment used is shown in Figure 10.

Sulfur dioxide gas was added until the final concentration was equivalent to 0.5% H_2SO_3. This mixture had an initial pH of 1.6. Steam introduced through an internal coil and the jacket brought the pressure and temperature up to an equivalent of 30 lbs. and 135°C respectively. The reaction mixture was held at this temperature and pressure for three hours, then cooled to 80°C and the mixture filtered. Filtration was very rapid producing a cake with above 40% solids and a light yellow liquor smelling slightly of SO_2 with approximately 8% dissolved solids, and a pH of 3.00.

This liquor was concentrated in a Rodney-Hunt evaporator to a syrup with 60% solids. Chemical analysis of the solids gave approximately 18% ash and 82% organics. Repeated production runs produced molasses of slightly varying analysis but usually within the range of the example shown.

The ash was high in iron (2.7%) and calcium (1.8%). The sodium, potassium and magnesium, content was typical of that found in natural products. It was low in phosphorus (0.005%) and high in sulfur, as would be expected because of sulfite residues.

The organics analyzed close to 3.5% nitrogen, which, when calculated as proteinaceous (6.25X) material, would be equivalent to almost 20% protein. However, when the protein content was reconciled against the total sugar analysis (40%), it became obvious that a portion of the nitrogen was in the form of amino-sugars and other non-protein nitrogen.

From subsequent runs, it appeared that when the total solids of the activated sludge was high in soluble solids, the sugar content of the molasses was high. On the other hand, when the soluble solids content was low, the sugar content was also low. An amino acid analysis on the organic molasses yielded:

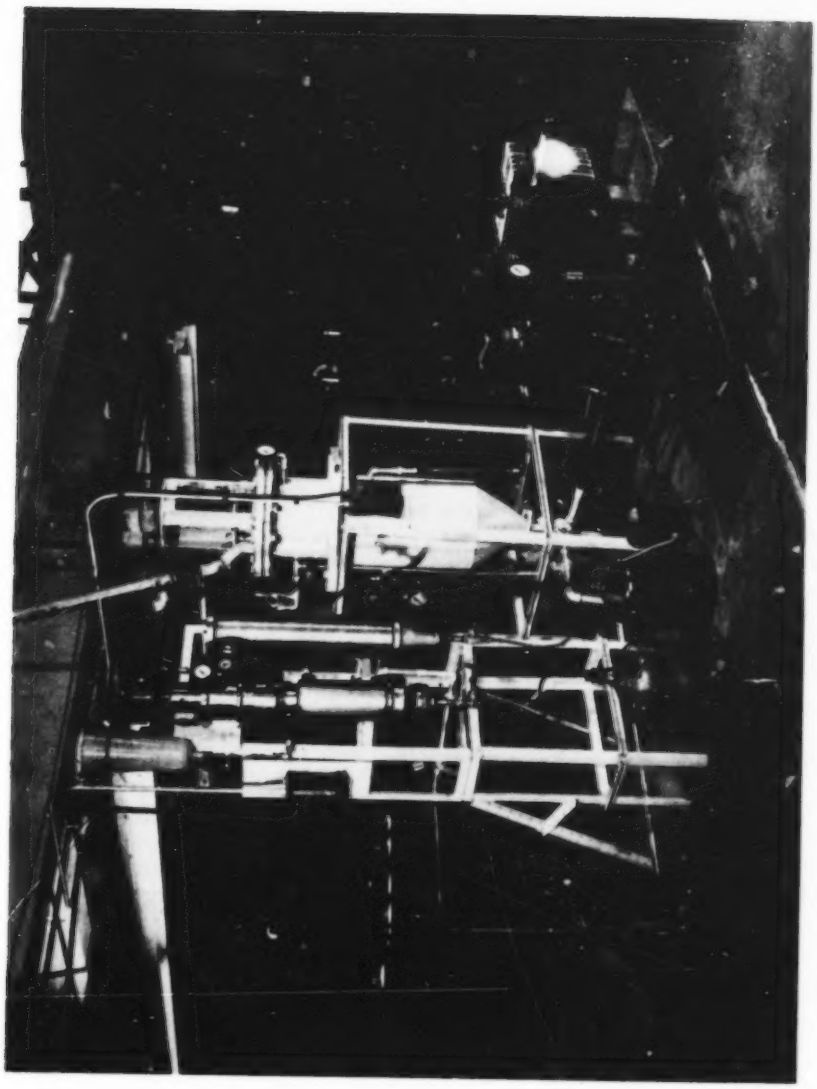


Fig. 10. Stainless Steel Pilot Plant Reactor for Sludge Digestion

FIGURE 11
Amino Acid Analysis on Organic Molasses

Amino Acid	Percentage
1. Arginine	0.79
2. Cystine	0.17
3. Glycine	1.88
4. Histidine	0.37
5. Isoleucine	1.08
6. Leucine	1.01
7. Lysine	0.87]
8. Methionine	0.36
9. Phenylalanine	0.74
10. Threonine	1.13
11. Valine	1.37

Cost Estimates for Sludge Disposition and Production of Organic Molasses

Based upon our experience in the laboratory and on batch-pilot runs, and relating this experience to production of the meat by-product, Peptone, and past experience in the sugar field, we have prepared preliminary cost factors for the production of organic molasses. These factors do not include the process improvements in dewatering–certainly a notable factor.

Essentially three operations are required:

(1) Cooking of sludge
(2) Filtration or separation of solids
(3) Concentration of extract to molasses

The principal expense will be involved in the cooking and concentration steps.

The cost of filtration will be a minor factor when compared to cooking and evaporation.

FIGURE 12
Economics for Production of Organic Molasses
(25,000 lbs. of Solids)

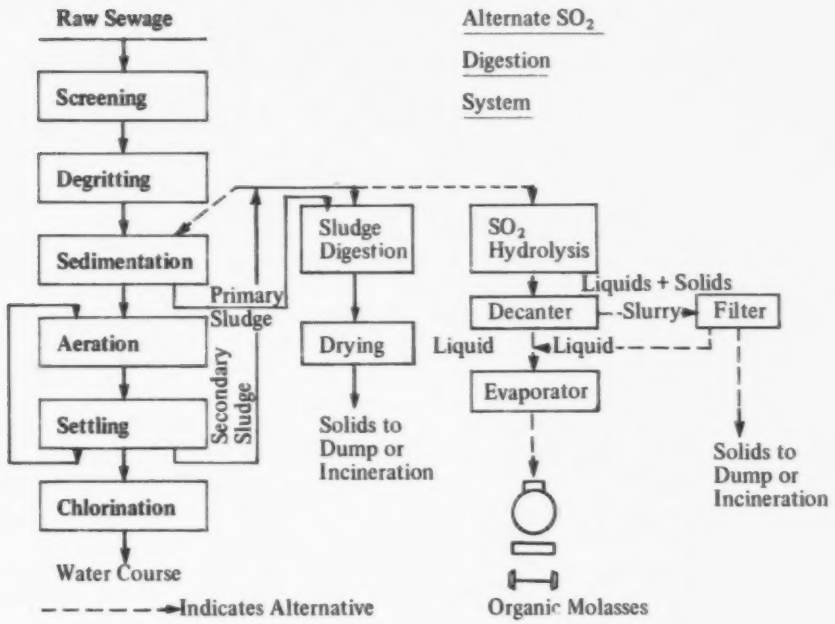
Digestion		Cost
(1)	35,000 lbs. Steam	$45.50
(2)	Water	.69
(3)	Electricity	1.50
(4)	Labor (16 man hours @$5.00)	80.00
(5)	Depreciation and use	33.00
		$160.69
Evaporation		
(1)	90,000 lbs. Steam	$117.00
(2)	Water	2.07
(3)	Electricity	5.10
(4)	Labor (17 man hours)	85.00
(5)	Equipment and depreciation	35.50
		$244.67
	Total Cost	$405.36

At this time, we feel the cost of digesting 25,000 lbs. of solids in stainless steel tanks, using direct steam (and SO_2) addition and yielding a syrup containing 20% solids, will cost $160.69 (this does not include the cost of the SO_2). Evaporation to molasses (50% solids) will cost an additional $244.67. Costs are itemized in Figure 12.

This brings our production costs to around .015 cents per pound of organic molasses.

A flow diagram of a possible plant for production of organic molasses is shown in Figure 13.

FIGURE 13
Activated Sludge Plant



THE NUTRITIONAL STUDY

The activation of sludge is, in reality, an aerobic fermentation process in which the organic matter in sewage is metabolized and assimilated as the nutrient media for the growth of microorganisms. In a sense this process is equivalent to the growth of single-celled proteins often suggested as feed sources. Dried activated sludge has been reported to be equal in nutritional quality, as measured by nitrogen retention in lambs, to soybean meal and urea-containing rations of similar crude protein content (8). However, the total nitrogen of a sludge-containing ration had an apparent lower digestibility in rats (52%) and a moderately low biological value (51%). Research into the nature of activated sludges has shown that the cell debris consists largely of polysaccharide polymers, protein, fat and inorganic complexes (9).

A preliminary experiment was performed to evaluate the utility of organic molasses in

animal feeds. The diets of each group supposedly contained sufficient protein, fat, carbohydrate, vitamins and salts to permit adequate growth. The diet of Group I contained 25% cornstarch. In Group II, the cornstarch was replaced by an equivalent quantity (on a dry weight basis) of the wet organic "molasses". In Group III, the cornstarch was replaced by an equivalent weight of non-digestible fiber. The study was designed to determine whether the organic molasses could replace the energy provided by the cornstarch.

To summarize this set of experiments, groups of rats fed organic molasses as part of their diet ate less food, had decreased body weights and greater organ weight/body weight ratios for several significant organs.

It appears that 25% organic molasses was excessive. The high moisture and high salt content were responsible for poor food utilization.

A second set of experiments was set up using less organic molasses (5% and 10%) and compared in the same trials with cane molasses at the same levels.

The seven synthetic diets tested were basically the same and are shown in Figure 14.

FIGURE 14
Synthetic Diets Used in Feeding Tests

Groups	Diet
1.	Ad lib sucrose control.
2.	5% organic molasses, sucrose replaced on dry weight basis.
3.	10% organic molasses, sucrose replaced on dry weight basis.
4.	5% cane molasses, sucrose replaced on dry weight basis.
5.	10% cane molasses, sucrose replaced on dry weight basis.
6.	Sucrose control, pair fed with 5% replacement groups.
7.	Sucrose control, pair fed with 10% replacement groups.

The efficiency of food utilization for weanling rats fed for 21 days is summarized in Figure 15.

FIGURE 15
Efficiency of Food Utilization (E.F.U.) for Weanling Rats Fed for 21 Days

Group		E.F.U.
1.	Surcrose Control	32.7
2.	Organic Molasses 5%	35.2
3.	Organic Molasses 10%	42.0
4.	Cane 5%	39.1
5.	Cane 10%	35.4
6.	Sucrose Control with 5% Pair Fed Groups	38.0
7.	Sucrose Control with 10% Pair Fed Groups	40.4

Gain in weight was greater for the 10% organic molasses group than for the other groups tested. Although the ad lib control group gained the next largest amount, it was on an unrestricted food intake and thus had the lowest E.F.U. of any group tested. In this respect, the E.F.U. of the organic molasses group was significantly greater than that of the ad lib control group, the 5% organic molasses and the 10% cane groups. The pair-fed control groups whose diets were exactly the same as the ad lib group had E.F.U. values significantly higher than the ad lib group. This may be due to the fact that scatter played a large part in recording intake of the unrestricted group. The inorganic molasses diets were less likely to scatter because of their more solid consistency.

All evidence indicates that organic molasses at the 10% level is an adequate energy substitute for cane molasses in the diet.

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